

Non-sintered electrode for an electrochemical generator with an alkaline electrolyte

5 The present invention relates to a non-sintered electrode such as that which is used in secondary electrochemical generators with an alkaline electrolyte, such as for example nickel-cadmium, nickel-iron, nickel-hydrogen, nickel-hydrogen-fixing metal accumulators. It also covers the generator containing such an electrode.

10 There are several types of electrode, in particular sintered and non-sintered electrodes, also called pasted or plasticized electrodes. The electrodes most widely used today are of the non-sintered type. Compared with other electrodes, a non-sintered electrode contains a greater quantity of active material, its volume capacity is thus increased and its production cost
15 lower.

 A non-sintered electrode consists of a support, serving as current collector, to which is applied a paste containing the active material and a binder, to which a conductive material is most often added. It is usually carried out by applying the paste in a porous three-dimensional conductive
20 support such as a felt or a foam, made of metal or carbon. For reasons of cost, there is now a move towards the use of two-dimensional conductive supports. The known binders used to produce an electrode with a three-dimensional support prove unsuitable for a two-dimensional support.

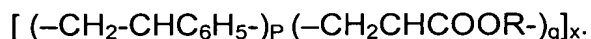
 Patent application EP 0 750 358 describes for example a non-sintered
25 nickel electrode the support of which is a corrugated metal sheet where teeth have been formed in order to fasten a microscopically irregular layer. A paste comprising carboxymethylcellulose (CMC) and a styrene/butadiene (SBR) copolymer is applied to this layer. In this case it was necessary to use a means other than the binder to ensure the mechanical behaviour of the
30 electrode,

 Also known is German patent application DE 19 709 107 which describes a nickel/metal hydride accumulator including an electrode formed

from a paste applied to a substrate. The paste contains an acrylate binder having 6 to 5 carbon ester groups.

The aim of the present invention is to propose an electrode, the mechanical behaviour and the mass capacity of which are at least equivalent to those of an electrode having a three-dimensional current-collecting support.

The subject of the present invention is a secondary electrochemical generator, with an alkaline electrolyte, containing a non-sintered electrode comprising a two-dimensional conductive support covered by a layer containing an electrochemically active material and a binder, characterized in that the said binder is a mixture of a cellulose compound and a styrene-acrylate copolymer of general formula:



The styrene-acrylate copolymer is a combination of elementary styrene units $(-\text{CH}_2-\text{CHC}_6\text{H}_5-)$ on the one hand, and elementary acrylic ester or acrylate units $(-\text{CH}_2\text{CHCOOR-})$ on the other.

The proportion of the styrene-acrylate copolymer is preferably less than 4% by weight of the active layer. When the proportion of styrene-acrylate copolymer is equal to or greater than 4% by weight of the active layer, the mass capacity of the electrode reduces perceptibly. In fact, an increase in the proportion of binder in the active layer means a reduction in the quantity of electrochemically active material, which causes a drop in performance values.

The proportion of styrene-acrylate copolymer is advantageously comprised between 0.15% and 3% by weight of the active layer. A reduction in the quantity of binder to a value below 0.15% by weight of the active layer does not reduce the capacity but the mechanical behaviour of the electrode is degraded.

The cellulose composition can be chosen in particular from methylcellulose (MC), carboxymethylcellulose (CMC), hydroxypropylmethylcellulose (HPMC), hydroxypropylcellulose (HPC) and hydroxyethylcellulose

(HEC). Carboxymethylcellulose (CMC) is further preferably used. The proportion of the cellulose compound is preferably comprised between 0.1 and 1% by weight of the active layer.

5 According to a particular embodiment of the present invention, the electrochemically active material comprises a nickel hydroxide. This hydroxide preferably has a spheroidal shape and has a grain size comprised between 7 μm and 20 μm .

 It is understood that the term "electrochemically active material
10 containing nickel hydroxide" used in the present application can mean a nickel hydroxide, a hydroxide containing principally nickel, but also a nickel hydroxide containing at least one syncrystallized hydroxide of an element chosen from zinc, cadmium and magnesium and at least one syncrystallized hydroxide of an element chosen from cobalt, manganese, aluminium, yttrium,
15 calcium, strontium, zirconium, copper. A syncrystallized hydroxide contained in the nickel hydroxide is a hydroxide forming a solid solution with the nickel hydroxide, i.e. occupying, in continuously variable proportion, the atomic sites defined by the crystal lattice of the nickel hydroxide.

 The active material can be covered by a coating based on cobalt oxide
20 or hydroxide optionally containing other elements such as nickel, zinc, aluminium and/or manganese, or else by a porous metal coating, of nickel for example.

 Nickel hydroxide is a not very conductive compound which necessitates the addition of a conductive material permitting a good electric
25 percolation. The active layer also contains a conductive material chosen from conductive particles, conductive fibres and their mixtures. The conductive particles can be chosen from carbon particles, metal particles, such as nickel for example, or the powder of a compound of a transition metal such as for example Co, CoO, Co(OH)₂, the mixed oxide of lithium and
30 cobalt LiCoO₂ and an oxide of conductive cobalt of a valency greater than 2. The said conductive fibres are chosen from carbon fibres, metal fibres or fibres covered with metal, such as nickel for example.

The active layer preferably contains a conductive compound constituted essentially by a compound of cobalt, preferably metal cobalt Co, cobalt oxide CoO, cobalt hydroxide Co(OH)₂, the mixed oxide of lithium and cobalt LiCoO₂ or an oxide of conductive cobalt of a valency greater than 2.

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The proportion of the conductive material in the active layer is advantageously between 3% and 15% by weight of the layer. Beyond this value, the volumetric capacity of the electrode decreases because of the proportional reduction in the quantity of active material.

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The active layer can also contain at least one other compound chosen from the compounds of zinc such as ZnO or Zn(OH)₂, yttrium such as Y₂O₃ or Y(OH)₃, ytterbium such as Yb₂O₃ or Yb(OH)₃, and calcium such as CaO, Ca(OH)₂ or CaF₂. This compound is usually added in powder form.

According to a first variant, the layer also contains a powder of a compound of yttrium, preferably yttrium oxide Y₂O₃ or yttrium hydroxide Y(OH)₃.

According to a first variant, the layer also contains a powder of a compound of ytterbium, preferably ytterbium oxide Yb₂O₃ or ytterbium hydroxide Y(OH)₃.

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The active layer advantageously also contains polymer fibres, such as for example polypropylene fibres. These fibres preferably have a length of 0.1 mm to 1.5 mm and a diameter of between 10 µm and 30 µm. These fibres are intended to strengthen the mechanical behaviour of the electrode.

By two-dimensional support is meant a flat support to which a paste is applied which, once dried, will form the active layer. The properties of the binder are thus essential in order to keep the active layer on the support, in particular in the case of spiralling of the electrode.

The said two-dimensional conductive support can be a solid or perforated strip, an expanded metal, a grid or a fabric. It is for example a strip of nickel steel having a thickness of between 10⁻² mm and 10⁻¹ mm, with a surface mass of between 0.3 g/dm² and 6 g/dm², with an aperture rate of between 0% and 80%, the diameter of the holes being between 0.1 mm and 3 mm.

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The subject of the present invention is also a secondary electrochemical generator comprising a positive electrode, a metal-hydride negative electrode and an aqueous alkaline electrolyte. The negative electrode can comprise in particular an active material chosen from cadmium and a hydrogen-fixing alloy.

Other characteristics and advantages of the present invention will appear during the following description of embodiments which are given by way of illustration but in no way limitative.

The single figure represents a sectional view of an electrode according to the invention. The electrode 1 is comprised of a plane-form conductive support 2 which fulfils the function of current collector. The support 2 is covered by an electrochemically active layer 3 which contains the electrochemically active material and a binder.

EXAMPLE 1

A first electrode (1) according to the invention is produced, the composition by weight of its active layer being:

Electrochemically active material based on $\text{Ni}(\text{OH})_2$	87.2%
Conductive material : $\text{Co}(\text{OH})_2$ powder	10%
Styrene-acrylate copolymer	2%
Cellulose compound: CMC	
0.3%	
Y_2O_3	0.5%

The powdery electrochemically active material is comprised of a nickel-based hydroxide containing the following additives: cobalt and zinc. The viscosity of the paste is adjusted with water. The paste is homogeneously deposited simultaneously on both sides of a two-dimensional metal support which is a perforated nickel steel strip 50 μm thick. The whole is then dried in order to eliminate the water, then laminated to the desired thickness and cut in order to obtain a positive electrode. Once the electrode is finished, the active layer displays a porosity of 30% and a grammage of 16 g/dm^2 .

EXAMPLE 2

A first comparative electrode (A1) is produced, with an active layer having the following composition by weight:

	Electrochemically active material based on Ni(OH)_2	88.2%
	Conductive material : Co(OH)_2 powder	10%
5	Binder: polytetrafluoroethylene (PTFE)	1%
	Cellulose compound: CMC	
	0.3%	
	Y_2O_3	0.5%

The powdery electrochemically active material is comprised of a nickel-based hydroxide containing the following additives: cobalt and zinc. The viscosity of the paste is adjusted with water. The paste is introduced into a three-dimensional support which is a nickel foam with a porosity of about 95%. The whole is then dried in order to eliminate the water, then laminated to the desired thickness and cut in order to obtain a positive electrode. Once the electrode is finished, the active layer displays a porosity of 30% and a grammage of 16 g/dm^2 .

EXAMPLE 3

An electrode (II) according to the invention is produced in the manner described in Example 1, with an active layer having the following composition by weight:

	Electrochemically active material based on Ni(OH)_2	86.9%
	Conductive material : Co(OH)_2 powder	10%
	Styrene-acrylate copolymer	2%
	Cellulose compound: CMC	
25	0.3%	
	Polypropylene fibres	0.3%
	Y_2O_3	0.5%

The powdery electrochemically active material is comprised of a nickel-based hydroxide containing the following additives: cobalt and zinc. Once the electrode is finished, the active layer displays a porosity of 30% and a grammage of 16 g/dm^2 .

EXAMPLE 4

A second comparative electrode (A2) is produced in the manner described in Example 2, with a layer having the following composition by weight:

	Electrochemically active material based on $\text{Ni}(\text{OH})_2$	79.9%
5	Conductive material : $\text{Co}(\text{OH})_2$ powder	10%
	Binder: polytetrafluoroethylene (PTFE)	1%
	Cellulose compound: CMC	
	0.3%	
	Polypropylene fibres	0.3%
10	Y_2O_3	0.5%

The powdery electrochemically active material is comprised of a nickel-based hydroxide containing the following additives: cobalt and zinc. Once the electrode is finished, the active layer displays a porosity of 30% and a grammage of 16 g/dm^2 .

15 EXAMPLE 5

An electrode (III) according to the invention is produced in the manner described in Example 1, with an active layer having the following composition by weight:

	Electrochemically active material based on $\text{Ni}(\text{OH})_2$	86.3%
20	Conductive material : $\text{Co}(\text{OH})_2$ powder	10%
	Styrene-acrylate copolymer	2.9%
	Cellulose compound: CMC	
	0.3%	
	Y_2O_3	0.5%

25 The powdery electrochemically active material is comprised of a nickel-based hydroxide containing the following additives: cobalt and zinc. Once the electrode is finished, the active layer displays a porosity of 30% and a grammage of 16 g/dm^2 .

EXAMPLE 6

30 An electrode (IV) according to the invention is produced in the manner described in Example 1, with an active layer having the following composition by weight:

	Electrochemically active material based on $\text{Ni}(\text{OH})_2$	84.9%
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	Conductive material : $\text{Co}(\text{OH})_2$ powder	10%
	Styrene-acrylate copolymer	4%
	Cellulose compound: CMC	
	0.3%	
5	Polypropylene fibres	0.3%
	Y_2O_3	0.5%

The powdery electrochemically active material is comprised of a nickel-based hydroxide containing the following additives: cobalt and zinc. Once the electrode is finished, the active layer displays a porosity of 30% and a grammage of 16 g/dm^2 .

EXAMPLE 7

An electrode (IV) according to the invention is produced in the manner described in Example 1, with an active layer having the following composition by weight:

15	Electrochemically active material based on $\text{Ni}(\text{OH})_2$	88.75%
	Conductive material : $\text{Co}(\text{OH})_2$ powder	10%
	Styrene-acrylate copolymer	0.15%
	Cellulose compound: CMC	
20	0.3%	
	Polypropylene fibres	0.3%
	Y_2O_3	0.5%

The powdery electrochemically active material is comprised of a nickel-based hydroxide containing the following additives: cobalt and zinc. Once the electrode is finished, the active layer displays a porosity of 30% and a grammage of 16 g/dm^2 .

Ni-MH accumulators are assembled, including respectively the previously manufactured electrodes A1, A2 and I to V. The negative electrode of known type has as electrochemically active material an intermetallic compound capable of forming a hydride once charged. Its capacity is greater than that of the positive electrode. Each positive electrode is placed beside a negative electrode from which it is isolated by a separator comprised by a nonwoven polypropylene fabric in order to form the

electrochemical bundle. The thus-spiralled bundle is inserted in a metal cup and impregnated with an alkaline electrolyte which is an aqueous alkaline solution comprised of a mixture of potassium hydroxide KOH 7.5N, sodium hydroxide NaOH 0.4 N and lithium hydroxide LiOH 0.5 N.

5 After a 48-hour rest at ambient temperature, an electric formation of the accumulators is carried out under the following conditions:

	Cycle 1:	rest 2h at 85°C;
		charge at 0.1I _c for 4h at 85°C, where I _c is the
10		current necessary to discharge the nominal
		capacity C of the generator in 1h;
		rest 2h at 20°C;
		charge 3h 0.33I _c ;
		discharge at 0.2I _c to a voltage of 0.9V;
		charge 40 minutes at I _c , then 1h 30 at 0.5I _c ;
15		discharge at 0.2I _c to a voltage of 0.9V.
	Cycles 2 to 10:	charge 16h 0.1I _c ;
		discharge at 0.2I _c to a voltage of 0.9V;
	Cycle 11:	charge 72 minutes I _c ;
		discharge at I _c to a voltage of 0.9V.

20 The mass capacities in cycle 11, relative to the mass of coated material, are listed in Table 1 below.

A mechanical behaviour test of the electrodes A1, A2 and I to V is then carried out as follows: each electrode is weighed, then released from a height of 50 cm onto a plane surface. The drop is repeated 10 times. Then the
 25 electrode is weighed again. The result of the test is expressed as the ratio of the initial mass less the final mass relative to the initial mass. The smaller this ratio, the more solid an electrode will be. The results obtained are shown in Table 1 below.

The two comparative electrodes A1 and A2 with three-dimensional
 30 support differ only in the presence in the active layer of polymer fibres, the role of which is to strengthen the mechanical behaviour of the electrode. The two electrodes behave in the same way during the mechanical behaviour test. It is noted that the mass capacity is identical for the two comparative

electrodes A1 and A2: the presence of 0.3% by weight of fibres in the active layer does not influence the electrochemical performance of the generator.

Similarly, electrodes I and II according to the present invention with two-dimensional support differ only in the presence of polymer fibres in the active layer. The capacity obtained in cycle 11 is of the same order for the two electrodes I and II, but it is seen that electrode II has a better mechanical behaviour than electrode I. The presence of 0.3% by weight of fibres in the layer does not influence the electrochemical performance of the generator.

The electrochemical evaluation of the generators assembled with electrodes according to the invention shows that electrodes I and II, including a two-dimensional conductive support and a binder according to the invention, present a mass capacity at least equal to that of electrodes A1 and A2 with three-dimensional support.

For a greater proportion of styrene-acrylate copolymer (electrode III) the capacity of the electrode reduces slightly. However, the increase in the proportion of binder permitted an improvement in the mechanical behaviour of the electrode despite the absence of fibres.

If the proportion of styrene-acrylate polymer is further increased (electrode IV), the mass capacity of the electrode falls because of the reduction in the quantity of active material.

Electrode V including a smaller proportion of styrene-acrylate copolymer displays a good mass capacity, but its degraded mechanical behaviour makes it more difficult to use.

TABLE 1

electrode	A1	A2	I	II	III	IV	V
support	foam	foam	strip	strip	strip	strip	strip
styrene-acrylate copolymer %)	1% PTFE	1% PTFE	2	2	2.9	4	0.15
cellulose compound CMC (%)	0.3	0.3	0.3	0.3	0.3	0.32	0.3
polypropylene fibres (%)	0.3	-	-	0.3	-	0.3	0.3
mechanical behaviour of the electrode (%)	0.2	0.2	1	0.2	0.3	0.15	5.1
generator output in cycle 11 (mAh/g)	239	240	242	245	235	220	244